

Ph.D. Thesis

**Ultrashort Pulsed Laser-Induced Chemistry:
Methodology, Instrumentation, and Analysis**

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Certificate of Original Authorship

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree. I also certify that the thesis has been written by me. Any and all help that I have received in my research work has been acknowledged. Finally, I certify that all information sources and literature used are indicated in the thesis.

Marcus Straw

Acknowledgements

The work presented in this dissertation was carried out under the supervision of Prof. Matthew Phillips, at the Microstructural Unit, Faculty of Science, University of Technology, Sydney, New South Wales, Australia. The work was performed within the Advanced Technology Group, Beam Technology R&D, FEI Company, Hillsboro, OR, U.S.A. I sincerely wish to thank Prof. Phillips for his guidance and support. I would also like to thank FEI Company for material support, Dr. Michael Lysaght for his support and flexibility, and Prof. Milos Toth for his review of my work and ongoing support throughout this process.

All work presented in the pages that follow was planned, coordinated, and managed exclusively by the author. As with any large project however, some degree of collaboration was required to achieve all that was achieved. I would like to take a moment here to explicitly acknowledge the work of those who contributed.

The instrumentation (see Figure 3.1) and experiments discussed in Chapter 3 were built and performed extensively by the author with the exception of the experiment using electron beam induced etching to illustrate the temperature dependence of surface adsorption (see Section 3.5.1). This experiment was suggested by Prof. Milos Toth and he did the EBIE work. The atomic force microscope line profiles shown in Figure 3.5 were collected by Dr. Steven Randolph.

The instrumentation (see Figure 4.1) and experiments detailed in Chapter 4 were likewise exclusively the work of the author with but two exceptions. First, the analysis of intensity data leading to the plot shown in Figure 4.5 was done by Dr. Jorge Filevich. Second, the author received a great deal of assistance from Dr. Steven Randolph setting up and learning to operate the quadrupole mass spectrometer portion of the instrumentation shown in Figure 4.10. Dr. Randolph was also instrumental in refining the subsequent experiments done to characterise the

by-products of the laser-induced plasma-mediated chemical reactions.

The development of the TripleBeam system has a long and storied history. It's hard to say definitively, but it is quite possible that the concept was first conceived by Dr. Mark Utlaut over a decade prior to the author's initial efforts. Dr. Utlaut was certainly the first to propose the idea within FEI Company and it is at FEI's world headquarters in Hillsboro, Oregon, USA that the earliest and the majority of the instrument's development has taken place. The first two prototypes of the tool were designed, built, and characterised almost exclusively by the author. The third and most current version has been a collaborative effort. The author's colleagues Mark Emerson, Dr. Steven Randolph, Dr. Jorge Filevich, and Dr. Aurélien Botman, as well as the author himself, all contributed variously to development of the LabView UI, alignment procedures, stage programming, beam stabilisation, contamination mitigation, optics, and beam delivery and control. In addition, elements of the most current design, particularly with regard to the laser injection port and the stage mount, were developed in collaboration with Dr. Tresa Pollock's group at the University of California, Santa Barbara in Santa Barbara, California, USA. This collaboration is discussed in more detail in Sections 5.6 and 5.7.

While the data collection and the segmentation work required to produce the three dimensional reconstruction of the geological sample presented in Section ref:sec:Gap was done solely by the author, the effort to quantify UPL-induced damage presented in the same section was a collaborative effort. Laser processing of tungsten carbide cobalt was done largely by Dr. Steven Randolph, while silicon processing was performed by the author. Transmission electron microscope and scanning transmission electron microscope analysis of these samples were performed by other FEI colleagues both in the U.S. and in Holland. Dr. Randolph also performed the electron backscatter diffraction analysis of UPL processed, single crystal copper discussed at the end of this section. Finally, the instrumentation, experiments, and analysis presented in Chapter 6 are the result of the collaborative efforts of the author and Dr. Randolph, and Dr. Randolph's contributions were considerable.

In addition to their critical technical support, I would like to offer special thanks to Dr. Steven Randolph, Dr. Mark Utlaut, Dr. Jorge Filevich, Dr. Milos Toth, and Dr. Aurélien Botman for the many, many useful discussions in which we engaged throughout this project's course.

Abstract

This dissertation explores the science and application of ultrashort pulsed lasers to locally induced chemical reactions having high spatial resolution. Chemical reactions driven in the gas phase by micro- to millimetre-scale plasmas formed when ultrashort pulsed laser ablation is performed in reactive gas atmospheres are studied via scanning electron microscopy, time-resolved optical emission spectroscopy, spatially resolved fast photography, plasma diagnostics, and mass spectrometry. Surface reactions resulting in metal deposition are explored via energy dispersive X-ray spectroscopy, electron backscatter diffraction, transmission electron microscopy, atomic force microscopy, and the use of a complex scientific instrument known as the TripleBeam designed and developed over the course of the project, and described in detail in this dissertation.

With wide scientific and industrial potential as both an experimental platform and a nanofabrication tool, the design and development of the TripleBeam instrument was initially motivated by the need to speed industrial processes currently employing focused ion beams. To that end, gas-phase ultrashort pulsed laser-induced chemistry was explored as a means of protecting sensitive components inside the instrument from material removed during in situ laser ablation. For this reason, reactions resulting in the transformation of solids to gas-phase compounds are targeted. However, a demonstration of the technique as a means for the fabrication of novel nanoparticles is also given.

Ultrashort pulsed laser-induced surface chemistries were explored with the hope of improving deposition rates and the purity of deposits made via electron and ion beam-induced processes. A previously unreported technique is presented in which electron-beam induced depositions provide templates for laser induced deposition, enabling both higher deposition rates and sub-diffraction limited pattern resolution.

With a rich potential application space driven by fundamental physics, ultrashort pulsed laser-induced chemistry can be seen as both an end in itself and as a means for exploring the complex interaction of light and matter. The work detailed in this dissertation produced methodologies, instrumentation, and analysis relevant to both the fundamental physics and the application of ultrashort pulsed-laser induced chemistry.

Contents

Certificate of Original Authorship	i
Acknowledgements	ii
Abstract	iv
List of Figures	ix
List of Tables	xiii
List of Symbols and Abbreviations	xiv
1 Introduction	1
1.1 Ultrashort Laser Pulses and Their Interaction with Matter	1
1.2 Thesis Structure	5
2 Pulsed Laser-Induced Processes in Various Ambient Environments	9
2.1 Introduction	9
2.2 Ablation	10
2.3 Deposition	24
3 Ultrashort Pulsed Laser Ablation in Reactive Gas Atmospheres	27
3.1 Introduction and Background	27
3.2 Model System	29
3.3 Instrumentation	30
3.4 Evidence of UPL Driven Chemistry	31
3.5 The Feasibility of a Surface Reaction: A Simple Analysis	35

3.5.1	The Temperature Dependence of Surface Adsorption and a Brief Foray into EBIE	39
3.6	Other Substrate/Precursor Systems Explored	42
3.7	Summary and Conclusions	44
4	Gas Phase Chemical Reactions Driven by UPLA-Induced Plasmas	46
4.1	Instrumentation	46
4.2	Procedure and Results	51
4.2.1	Characterisation of the Plasma	61
4.2.2	Reaction By-Products	66
4.3	Conclusions	69
5	TripleBeam Design and Development	71
5.1	Introduction	71
5.2	Overview	71
5.3	Laser	73
5.3.1	Erbium Doped Fibre Oscillator	74
5.3.1.1	Mode-locking	75
5.3.1.2	Group Velocity Dispersion	80
5.3.2	Chirped Pulse Amplification and the Regenerative Amplifier	82
5.4	DualBeam [™]	90
5.4.1	FIB	92
5.4.2	SEM	96
5.5	Analysis Techniques	99
5.5.1	Energy Dispersive X-ray Spectroscopy	100
5.5.2	Electron Backscatter Diffraction	101
5.6	Integration	102
5.6.1	Beam Delivery	105
5.6.2	Beam Control	108
5.6.3	Beam Stability/Auto Alignment	111
5.6.4	Sample Control	115
5.6.5	Contamination Mitigation	117
5.6.6	Ongoing Development Effort	119
5.7	Instrument Characterisation and Validation	119

5.7.1	The Need for 3D and the Gap in Length Scales	120
5.7.2	A Tool for Bridging the Gap	123
5.8	Conclusion	134
6	Laser-Induced Surface Chemistry	135
6.1	Introduction and Background	135
6.1.1	Photolysis	137
6.1.2	Pyrolysis	139
6.2	Instrumentation: A Note on Gas Delivery	144
6.3	Experimental Background	146
6.4	LID: Procedure and Results	148
6.5	EBID Templated LID: Ongoing Efforts	157
6.6	Summary and Future Work	164
6.6.1	Non-Templated LID	164
6.6.2	EBID Templated LID	166
7	Summary and Concluding Remarks	168
	Bibliography	175

List of Figures

1.1	A timeline of the complex processes involved in ultrashort pulsed laser ablation	6
2.1	Silicon microstructures formed via ultrashort pulsed laser processing in an SF_6 atmosphere	14
3.1	Experimental arrangement for study of laser ablation in reactive gas atmospheres	32
3.2	$100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ pits machined in SiO_2	33
3.3	$100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ pits machined in N_2	34
3.4	Possible adsorbate mediated scenarios for UPLA driven reaction in the model system.	37
3.5	AFM line profiles of etch pits in SiO_2 generated by XeF_2 -mediated EBIE	40
3.6	$100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ pits machined in SiO_2 heated to 150°C	41
3.7	SEM image of nanoparticles generated by laser ablation of SiC in XeF_2	45
4.1	Direct spatio-temporal analysis	47
4.2	Intensified CCD schematic	49
4.3	Time-resolved optical emission spectra of SiO_2 ablated in Xe and XeF_2	52
4.4	Composite, time-resolved CCD images of plasma plume expansion into N_2 and XeF_2 atmospheres	55
4.5	Time-resolved integrated intensity of the 390.55 nm emission from Figure 4.4	58
4.6	Model of plume expansion into a background gas	59

4.7	Modelled versus measured values of plume expansion into N ₂ and Xe ₂ atmospheres	60
4.8	An example of the Boltzmann plot method used for measuring electron temperature T_e of a plasma	64
4.9	Si ion lines used to measure n_e	65
4.10	Arrangement of the mass spectrometer used to characterise reaction by-products	67
4.11	RGA analysis of by-products produced when the plasma generated during ultrashort pulsed laser ablation of SiO ₂ interacts with XeF ₂ in the gas phase	68
4.12	The reaction pathway for the formation of fluorinated silicon compounds during UPL ablation of SiO ₂ in a XeF ₂ atmosphere	70
5.1	The TripleBeam System	72
5.2	Main sub-components of the TripleBeam's laser	74
5.3	Longitudinal modes supported by a laser system	76
5.4	Additive pulse mode-locking schematic	79
5.5	Generalised polarisation APM schematic	80
5.6	Erbium doped fibre oscillator design	82
5.7	Typical grating-based stretcher configuration used in laser amplifiers that employ chirped pulse amplification	84
5.8	A schematic of the energy states of bound electrons in a Ti:Sapphire crystal used as the gain medium in a regenerative laser amplifier . . .	86
5.9	Detailed schematic of the TripleBeam laser's upper level including the Nd:YAG pump laser and the regen cavity	87
5.10	Gain curve resulting from the amplification of a hypothetical pulse illustrating gain saturation	89
5.11	Oscilloscope traces of actual laser pulses transiting a Ti:Sapphire gain medium	89
5.12	Typical grating-based compressor configuration	90
5.13	Evolution of a pulse as it progresses through a chirped pulse amplification laser system	91
5.14	An example of ion channelling	93
5.15	A typical gallium liquid metal ion source	94

5.16	Electron-sample interactions	99
5.17	Atomic orbitals K, L, and M	100
5.18	Electron backscatter diffraction	103
5.19	Kikuchi lines from a copper sample	104
5.20	Schematic of the TripleBeam layout and the general beam path of the laser	106
5.21	Specimen chamber of the TripleBeam system	107
5.22	The laser injection port of the TripleBeam system as mounted on the instrument	108
5.23	Output of the scan field distortion routine used to determine the extent of the scan field as well as the area over which the lens produces a usable spot	109
5.24	A screen-shot of the LabView UI developed to communicate with the laser and the FSM	110
5.25	A simplified slice-and-view routine illustrating how computer control of the laser and FSM are integrated with computer control of the DualBeam	111
5.26	The two-levels of the beam stabilisation system	113
5.27	The actual path the beam takes through the lower level of the beam stabilisation system	114
5.28	The TripleBeam system's custom stage	116
5.29	The effect of detector saturation due to "gentle" ablation being per- formed during SEM imaging	118
5.30	Geometry used for FIB serial sectioning	122
5.31	A three dimensional reconstruction of a 3.6 million μm^3 geological sample serially sectioned with the laser in 200 nm slices	125
5.32	SEM micrographs of bulk material removal on a WC-Co sample via UPL as performed on the TripleBeam system	126
5.33	An analysis of a laser polished WC-Co sample	127
5.34	Electron diffraction analysis of laser polished WC-Co	128
5.35	TEM analysis of the heat affected zone in UPL machined silicon . . .	129
5.36	EBSD analysis of features laser machined at a range of fluences and with both single and multiple shots per feature	133

6.1	Potential energy versus internuclear distance of a molecular system's vibrational states	138
6.2	Pathways for dissociation of molecules with photo-excited electronic structures	139
6.3	On-stub gas delivery assembly	145
6.4	Deposition rate data used to calibrate the gas field produced by the custom, on stub gas delivery system	146
6.5	Dendritic Pt structures formed via LID of $\text{Pt}(\text{PF}_3)_4$	148
6.6	A comparison of EDS analysis of laser-induced platinum deposition on gold to a reference spectrum taken of gold with no laser-induced platinum deposition and a spectrum of platinum deposited on silicon via EBID	151
6.7	A comparison of EDS analysis of laser-induced platinum deposition on black glass to a reference spectrum taken of black glass with no laser-induced platinum deposition and a spectrum of platinum deposited on silicon via EBID	152
6.8	Ultrashort pulsed laser-induced platinum deposits on gold and black glass using $\text{Pt}(\text{MeCp})\text{Me}_3$ as the precursor	153
6.9	A serpentine pattern of 60 to 70 nm wide Pt lines deposited via EBID templated LID demonstrating the ability to produce sub-diffraction limited features using this technique.	158
6.10	Deposited volume of EBID templated laser-induced deposition as a function of EBID dose	159
6.11	AFM images of EBID templated laser-induced deposition of Pt on gold and SiO_2/Si substrates	160
6.12	AFM images of the morphologies of the deposits on gold and on the SiO_2/Si substrate	163
6.13	AFM images of an EBID templated LID of Pt straddling a gold- SiO_2 interface illustrating the differences in both morphology and deposition rate	164

List of Tables

4.1	Wavelength, energy levels, probability, and transition configurations of Si lines observed during LIBS	53
4.2	Table of XeF* excimer states, their electronic configurations, radiative transitions, and lifetimes.	54
6.1	Single pulse and steady state sample heating results modelled using different laser fluences and repetition rates	143
6.2	Substrates, laser powers, and results of attempted LID	150

List of Symbols and Abbreviations

α	optical absorption coefficient
$\Delta\tau$	ICCD gate delay
ν	photon frequency
ν_L	laser repetition rate
ϕ	laser fluence
ϕ_{th}	threshold laser fluence at which ablation occurs
τ_e	electron cooling time
τ_i	lattice heating time
τ_p	laser pulse duration
c	the speed of light
h	Planck's constant
k_B	Boltzmann constant
n_e	electron density
T_e	electron temperature
T_i	lattice temperature
v_g	group velocity
v_p	phase velocity

E_p	laser pulse energy
a.u.	arbitrary units
AFM	atomic force microscope
APM	additive pulse mode-lock
BSD	backscattered electron detector
BSE	backscattered electrons
BSS	beam stabilisation system
CPA	chirped pulse amplification
CW	continuous wave
EBID	electron beam-induced deposition
EBIE	electron beam-induced etching
EBSD	electron backscatter diffraction
EBSP	electron backscatter pattern
EDS	energy dispersive X-ray spectroscopy
ESEM	environmental scanning electron microscope
ETD	Everhart-Thornley secondary electron detector
FSM	fast steering mirror
GIS	gas injector system
GVD	group velocity dispersion
HAZ	heat affected zone
IBID	ion beam-induced deposition
IBIE	ion beam induced-etching

ICCD intensified charge coupled device

LCE laser chemical etch

LIBS laser-induced breakdown spectroscopy

LID laser-induced deposition

LIP laser injection port

LIPPS laser-induced periodic surface structures

LMIS liquid metal ion source

LTE local thermodynamic equilibrium

MCP microchannel plate

NA numerical aperture

ND neutral density

Nd:YAG neodymium-doped yttrium aluminium garnet laser gain medium

PE primary electrons

PLA pulsed laser ablation

RGA residual gas analyser

SE secondary electrons

SED secondary electron detector

SEM scanning electron microscope

SF₆ sulphur hexafluoride

SHG second harmonic generation

SiO₂ silicon dioxide

TE thermodynamic equilibrium

TEM transmission electron microscope

THG third harmonic generation

Ti:Sapphire titanium doped monocrystalline sapphire (Al_2O_3) laser gain medium

UI user interface

UPL ultrashort pulsed laser

UPLA ultrashort pulsed laser ablation

XeF_2 xenon difluoride